# Synopsis

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Water soluble polymers are specialty polymers with applications in various industries They are used in the water treatment industry, paper, mineral processing, textile and pharmaceutical industries They are also used in the formulation of detergents, personal care products, petroleum production, enhanced oil recovery, paints and in the formulation of surface coatings They are usually discarded from industries in to waste water or dumped in landfills Thus creates environmental issues regarding toxic effects and also poses accumulation problems The degradation of polymers depends on many factors like the mode of degradation and chemical structure The degradation could be random chain scission, unzipping or breakage at the bond with lowest energy Thus it becomes imperative to determine the kinetics of degradation of these polymers to design better methods for the removal from the environment

In the present investigation, the degradation of three commercially important water soluble polymers has been investigated using different modes The polymers studied are poly(ethylene oxide) (PEO), polyacrylamide (PAM) and poly(vinyl alcohol) (PVA) While PEO is a simple polymer with only carbon, hydrogen and oxygen in its backbone, PAM and PVA have pendant amide and hydroxyl groups, respectively The degradation was studied under ultrasonic irradiation, UV and pulsed laser irradiation, by thermal and microwave heating and by pyrolysis The kinetics of these reactions was determined by applying continuous distribution models

The ultrasonic degradation of polyacrylamide and polyethylene oxide in solution was studied at different temperatures The time variation of the number average molecular weight was determined using gel permeation chromatography Continuous distribution kinetics was used to determine the degradation rate coefficients The degradation rate coefficient decreased with increasing temperature and was attributed to higher vapor pressure and lower viscosity at higher temperatures The ultrasonic degradation of poly(ethylene oxide) of different initial molecular weights was studied at a fixed temperature The ultrasonic degradation rate, $\kappa$, was assumed to be of the form, $\kappa = k_d (x - x_{lim})^{\lambda}$, where $k_d$ represents the rate coefficient, while x and $x_{lim}$ represent the molecular weight and limiting molecular weight, respectively A continuous distribution model assuming midpoint chain scission and two different expressions for the rate coefficient was developed to satisfactorily model the experimental data In the first method, the model was solved numerically and the values of $k_d$ and $\lambda$ were determined by fitting the model to the experimental data However, when $\lambda$ is assumed to be unity, an analytical solution to the model was determined and fitted the experimental data for the degradation of PEO To confirm this model, the effect of initial molecular weight on the degradation of other polymers polyacrylamide, poly(butyl acrylate), poly(methyl acrylate) was also investigated The assumption of $\lambda$ =1 fitted the experimental data for the ultrasonic degradation of these polymers indicating that this is a reasonable approximation for the ultrasonic degradation of polymers The effect of various solvents on the degradation of poly(ethylene oxide) was also investigated No degradation was observed when PEO was degraded in acetone, acetonitrile or methanol but degradation occurred in mixtures of water and the above solvents Thus the degradation of PEO was dependent more on the vapor pressure of the solvent than on polymer-solvent interactions The ultrasonic degradation of poly(vinyl alcohol) was investigated at different pH of solvent, in different water/solvent binary mixtures and at different polymer concentrations Higher degradation rate was obtained at extremes of pH, in better solvents (where PVA remained in extended conformation) and at lower polymer concentration However, no effect of temperature or vapor pressure was observed on the ultrasonic degradation of PVA This indicates that unlike the degradation of PEO or

PAM, the degradation of PVA is dependent on the polymer-solvent interactions rather than on vapor pressure

The photocatalytic degradation of poly(ethylene oxide) and polyacrylamide was investigated using combustion synthesized nano-sized $TiO_2$ catalyst (CSN- $TiO_2$) The degradation was conducted with two different UV lamps of 125 and 80 W Degradation of PEO was observed in both the cases whereas PAM degraded only when exposed to lamp of higher power even in the presence of catalyst Continuous distribution kinetics was applied to determine the kinetics of the photodegradation process The degradation rate coefficients of the polymers in the presence of combustion synthesized $TiO_2$ were higher than the degradation rate coefficients obtained with commercially available $TiO_2$ (Degussa P-25) The enhanced degradation rate of the polymers when catalyzed by CSN-$TiO_2$ can be due to the nano-size, high surface area and the presence of hydroxyl groups on the surface of the catalyst However, the catalyst had no effect on the photodegradation of poly(vinyl alcohol) in aqueous solution The degradation of PVA under UV exposure was studied at different pH values and on the addition of potassium chloride and potassium dichromate The photodegradation rates under UV exposure were highest at extremes of pH and the degradation rates were highly enhanced in the presence of potassium chloride and potassium dichromate

The kinetics of degradation of polyethylene oxide, polyacrylamide and poly(vinyl alcohol) was investigated using a pulsed Nd YAG laser, operating at 266 nm wavelength with ~6 ns pulses Continuous distribution kinetics for random chain scission was used to obtain the rate coefficient for the degradation process. A pathway for degradation has been proposed based on the experimental observations The significance of polymer concentration and the laser light intensity along with the requirement of oxygen for degradation has been correlated to the mechanism of the degradation process The degradation was found to decrease with increasing polymer concentration while a threshold light intensity was required to initiate the degradation process

The kinetics of the thermal and microwave assisted oxidative degradation of poly(ethylene oxide) and polyacrylamide in solution was determined with potassium persulfate as the oxidizing agent The degradation was studied as a function of temperature and persulfate concentration and it was found that the degradation rate

increased with temperature and concentration of persulfate Continuous distribution kinetics was used to determine the rate coefficients for the degradation process and the activation energies were obtained The results indicate that microwave assisted process has a lower activation energy compared to that for thermal degradation The degradation of poly(ethylene oxide) and polyacrylamide in aqueous solution was also studied with ascorbic acid The results showed that the degradation of polymers is significantly enhanced in the presence of ascorbic acid The degradation rate initially increased with ascorbic acid concentration, but was independent of the acid concentration at high acid concentration A model based on continuous distribution kinetics showed that the experimental data matched well with theory

The effect of five different metal oxides on the pyrolysis of PEO, PAM and PVA was investigated using thermogravimetry The presence of metal oxide did not influence the degradation of PEO while the order of metal oxide on the degradation rate of PAM and PVA was PbO > $Co_3O_4$> CuO > ZnO > $Al_2O_3$ The miscibility and the decomposition of PEO-PAM and PVA-PAM blend were also investigated The blends were found to be immiscible and the presence of one polymer did not influence the degradation of the other polymer in the polymer blend.

Thus, in the present work, the degradation of three water soluble polymers has been investigated by various methods In each case, continuous distribution kinetics has been applied to determine the rate coefficients from the experimental data